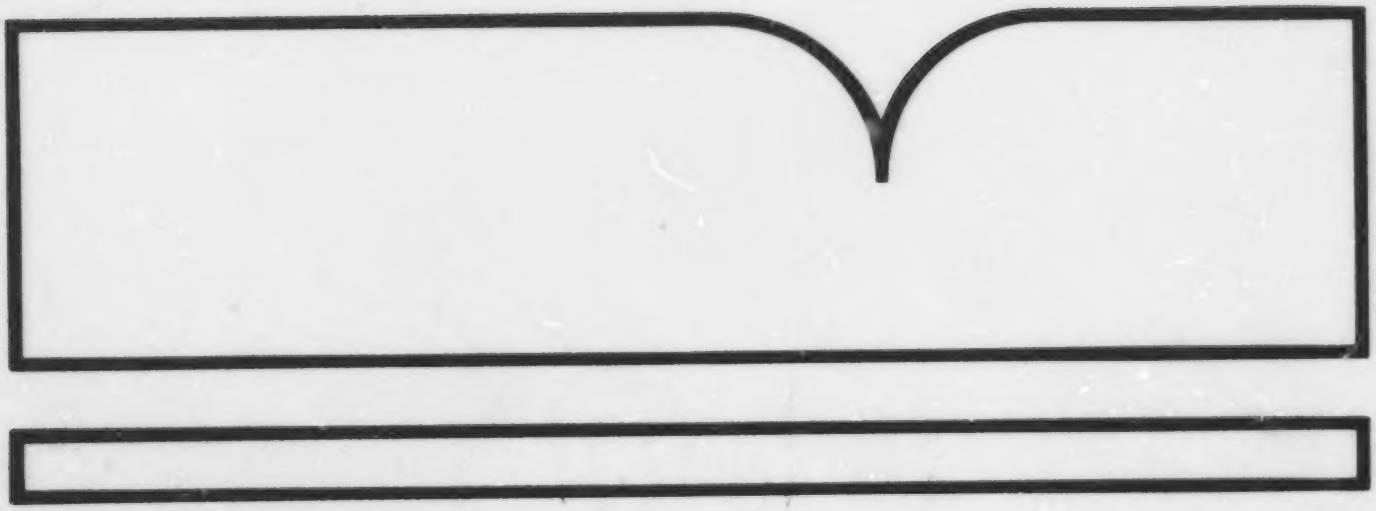
PB86-190063

Abiotic Transformation of Organic Chemicals at the Particle/Water Interface

(U.S.) Environmental Research Lab., Athens, GA

Apr 86



U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-190063

EPA/600/D-86/086
April 1986

ABIOTIC TRANSFORMATION OF ORGANIC CHEMICALS AT THE PARTICLE/WATER INTERFACE

by

Richard G. Zepp and N. Lee Wolfe
Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, GA 30613

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GA 30613

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-86/086		PB86 190063/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
ABIOTIC TRANSFORMATION OF ORGANIC CHEMICALS AT THE PARTICLE/WATER INTERFACE	April 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Richard G. Zepp and N. Lee Wolfe	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency Athens, GA 30613	ANBW1E
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Research Laboratory - Athens GA Office of Research and Development U.S. Environmental Protection Agency Athens, GA 30613	Book chapter
	14. SPONSORING AGENCY CODE
	EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Heterogeneous reactions are important contributors to the transformation of organic chemicals in the environment and are increasingly being used in the treatment of polluted water. Kinetic models are presented here that describe selected environmentallly relevant thermal and photochemical reactions in particle/water systems, including reactions in approximately equilibrated heterogeneous systems and in systems involving reactive site saturation. The effects of slow intersite diffusion on heterogeneous reactions are discussed as are recent models that describe the kinetics of such processes.

To illustrate the application of the kinetic models, examples are provided of kinetic treatments of thermal and photochemical reactions involving organic chemicals in aqueous suspensions of sediments, metal oxides, or algae. Thermal reactions that are discussed include the hydrolysis of sorbed organic chemicals and the reduction of organic compounds in anaerobic sediments. Kinetic relations that govern photoreactions in particle suspensions are discussed and illustrative examples are provided of direct photoreactions of surface complexes in metal oxide suspensions; semiconductor mechanisms for photochemical redox processes; and photosensitized reactions on surfaces of algae, sediments, and soil surfaces.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	52
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABIOTIC TRANSFORMATION OF ORGANIC CHEMICALS AT THE PARTICLE/WATER INTERFACE

Richard G. Zepp and N. Lee Wolfe
Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, Georgia 30613

"It is only after you have come to know the surface of things that you can venture to seek what is underneath. But the surface of things is inexhaustible."

-- Italo Calvino, "Palomar", 1983

Abstract

Heterogeneous reactions are important contributors to the transformation of organic chemicals in the environment and are increasingly being used in the treatment of polluted water. Kinetic models are presented here that describe selected environmentally relevant thermal and photochemical reactions in particle/water systems, including reactions in approximately equilibrated heterogeneous systems and in systems involving reactive site saturation. The effects of slow intersite diffusion on heterogeneous reactions are discussed as are recent models that describe the kinetics of such processes.

To illustrate the application of the kinetic models, examples are provided of kinetic treatments of thermal and photochemical reactions involving organic chemicals in aqueous suspensions of sediments, metal oxides, or algae. Thermal reactions that are discussed include the hydrolysis of sorbed organic chemicals and the reduction of organic compounds in anaerobic sediments. Kinetic relations that govern photoreactions in particle suspensions are discussed and illustrative examples are provided of direct photoreactions of surface complexes in metal oxide suspensions; semiconductor mechanisms for photochemical redox processes; and photosensitized reactions on surfaces of algae, sediments, and soil surfaces.

1. INTRODUCTION

During the past decade studies of heterogeneous chemistry involving various types of particles in water have burgeoned. This interest is reflected in the recent decision of the American Chemical Society to publish the journal Langmuir, which is entirely devoted to surface chemistry. A major impetus for environmentally related research in this area has been the need for reliable estimates of the lifetimes of pollutants in surface water and groundwater. Interest in the kinetics of metal oxide dissolution as related to fields of aquatic geochemistry and chemical oceanography/limnology also has prompted a number of recent studies dealing with the chemistry of organic chemicals adsorbed on oxides in water. In atmospheric research concern over toxic effects of precipitation has lead to investigations of heterogeneous reactions in cloud droplets and aqueous aerosols. In addition, the energy crisis of the mid-1970's stimulated research on the development of heterogeneous photocatalytic processes that can be used to capture solar energy. Such photocatalytic processes also have been applied to oxidize pollutants in wastewaters.

In this chapter we discuss only a portion of the research in this active area. Primary emphasis is on the kinetics of abiotic transformations of organic chemicals in particle/water systems that are relevant to surface waters. Our considerations are further limited to conditions in which reactant concentrations are typical of those usually encountered in aquatic environments, i.e., less than 10 micromolar and/or below the aqueous solubility limit.

The predominant sorbents of organic solutes in freshwater systems are sediments. Sediments are mixtures of inorganic minerals that are usually associated with organic and inorganic polyelectrolytes. A substantial part of the sediments in freshwaters is derived from soil runoff. Thus, the abiotic transformations of organic chemicals in sediment/water as well as

soil/water mixtures receive a major emphasis. In addition, photoreactions involving algae and certain metal oxides are discussed, because such particles are important components of the suspended matter in lakes.

Heterogeneous chemical reactions in aqueous systems involve the partitioning of the substrate between water and one or more other phases. Estimation of the extent of partitioning of micropollutants to non-aqueous phases such as sediments, biota, colloidal organic substances, and surface films has been and continues to be the subject of much current research. Here we refer to the partitioning of a solute from water onto an aquatic particle as "sorption". Sorption includes partitioning to particle interiors as well as to the surface itself.

Our discussion of heterogeneous reactions is organized under three topical areas. First, we consider the kinetic models and equations that describe thermal and photochemical reactions on aquatic particulates. Then we present a detailed examination of two types of organic heterogeneous reactions that are significant in aquatic environments, hydrolysis and reduction. Finally, we discuss the kinetics and types of organic heterogeneous photoreactions of environmental interest, covering both direct and indirect photoprocesses.

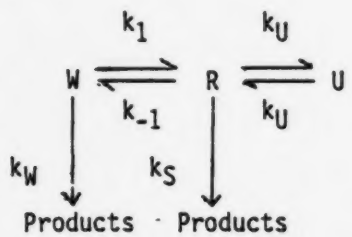
2. KINETIC MODELS AND EQUATIONS

Our discussion begins with the simplest case, a description of multiphase reaction kinetics in equilibrated systems. Then, we examine more complex models that apply to heterogeneous reactions in nonequilibrated systems. For purpose of illustration, only the simplest models that apply to this vast research area are discussed here. Useful discussions of heterogeneous catalysis can be found in a monograph by Clark (1970). Laidler and Bunting's (1973) treatments of enzyme kinetics also provide a relevant extension to our discussions.

2.1 Heterogeneous Kinetics in Equilibrated Systems

A reactive organic chemical, or "reactant," in an aqueous suspension of natural particles is likely to be distributed into several different phases each of which influences the reaction kinetics. Here we assume that the movement of reactant from one phase to another is much more rapid than chemical reaction and that the system is approximately at equilibrium. More detailed discussions of equilibrium sorption are provided in Westall's (1986) chapter on adsorption mechanisms and in a recent paper by Karickhoff (1984).

For illustration, consider a model system in which a chemical is distributed among three rapidly equilibrated phases, one of which is water and the other two of which are components of a natural particle, two particles with differing reactivities, etc. The chemical reacts in water and in one of the two particle phases. Reaction rates are assumed to be first-order with respect to reactant concentration.



(1)

In eq. 1, W represents aqueous phase reactant, R denotes reactant sorbed in a phase where reaction occurs, and U denotes reactant sorbed in an unreactive phase. The first order rate constants, k_W and k_S, correspond to reaction in aqueous and sorbed states, respectively. It is further assumed in this case that no interactions occur among sorbed reactant molecules and that an infinite number of reactive sites are available on the particle. In a subsequent section, the effect of site saturation will be considered.

The fraction of reactant residing in a given phase, j, at equilibrium is:

$$F_j^e = \rho_j K_j / \sum_i \rho_i K_i \qquad (2)$$

where K_i are partition coefficients that equal the ratio of concentrations in phase i to the concentration in some reference phase and ρ_i are the relative amounts of the two phases. If water is selected as the reference phase then ρ_W and K_W for the reactant in aqueous phase W are unity and

$$\sum_i \rho_i K_i = 1 + \rho_R K_R + \rho_U K_U$$

The concentration C_j (expressed as amount per system volume) in a given phase, j, at equilibrium equals $F_j^e C_T$ where C_T is the total concentration. It follows that the rate of chemical reaction, $-dC_T/dt$, denoted by v, is expressed by:

$$v = C_T(F_W^e k_W + F_R^e k_R) \qquad (3)$$

Note that the term in the rate expression that is attributable to reaction in a given phase is "retarded" by the factor F_j^e. If the rate constant for reaction on the particle is less than that for reaction in aqueous solution, i.e., if $k_R < k_W$, the net effect of sorption onto natural particles is a reduction in the chemical reaction rate compared to that in pure water.

Through generalization of this model to a system that includes a total of "i" equilibrated phases with varying reactivities, it can be shown that v is described by:

$$v = C_T \sum_i F_i^e k_i \qquad (4)$$

where k_i are first-order rate constants for reaction in phases i. Under the equilibrium assumption, the observed disappearance rate in any phase must equal the total disappearance rate.

The neutral hydrolysis of the organophosphorothioate insecticide, chlorpyrifos, provides a good example of an organic transformation in an equilibrated sediment-water system (Figure 1) (Macalady and Wolfe, 1985). The kinetic data in both the aqueous phase and sediment phase are described by first-order rate

expressions. Computer analysis of the concentration-time data in both phases indicated that sorption and desorption of chlorpyrifos were considerably more rapid than hydrolysis. The constancy of the ratio of sorbed to dissolved reactant in this system is another indication that the two phases are equilibrated during the reaction, although such a constant ratio could also result even if the system was not equilibrated. (See following discussion of steady-state model.)

2.2 Kinetic Models Involving Site Saturation

The preceding section described equilibrium models that assumed unlimited reaction sites on particles. Many studies of heterogeneous reactions, however, have shown that site limitation must be taken into account in any general description of reaction kinetics. Langmuir's pioneering studies (Gaines et al., 1983) in the case of heterogeneous catalysis of gas phase reactions were the first to develop the concept of site saturation.

A number of kinetic situations can develop that require consideration of site saturation. Here, for illustration, we consider the simplest case:

$$W \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R \xrightarrow{k_s} \text{Products} \qquad (5)$$

In this case phase R is assumed to have a limited number of reaction sites and the products are assumed to rapidly leave the surface. If θ denotes the fraction of reactive sites that are occupied and R_t denotes the total concentration of sites then rate equations 6 and 7 describe the kinetic model:

$$v = k_s C_R \qquad (6)$$

$$\frac{dC_R}{dt} = k_1 (1 - \theta) R_t C_W - k_{-1} C_R - k_S C_R \qquad (7)$$

As reaction proceeds, the concentration of sorbed reactant reaches a steady state and dC_R/dt becomes nearly zero. Under these conditions:

$$C_R = \frac{k_1 (1 - \theta) R_t C_W}{k_{-1} + k_s} \qquad (8)$$

By substitution of $\theta = C_R/R_t$ and of eq 8 into eq 6, it can be seen that:

$$v = \frac{k_1 k_S R_t C_W}{k_{-1} + k_S + k_1 C_W} \qquad (9)$$

Both algal-induced photoreaction of aniline (Figure 2) and the photodissolution of the iron oxide, lepidocrocite (Figure 3), are examples of heterogeneous reactions that exhibit the hyperbolic relationship described by equation 9. These reactions are discussed later in more detail.

Equation 9 simplifies under two conditions. When reactant concentration is sufficiently large that $k_1 C_W$ is much larger than $(k_{-1} + k_S)$, the rate becomes zero order with respect to reactant concentration. Under these conditions all the reactive sites are "saturated." The maximum rate is proportional to the rate constant for reaction of substrate sorbed on reactive sites as well as to the total concentration of such sites. The latter is proportional to the particle/water ratio, ρ, as well as the site density. Smaller particles, with their higher surface area to mass ratio, are expected to exhibit a higher Rt/ρ ratio than larger particles.

On the other hand, with very low reactant concentrations, such that $(k_{-1} + k_S)$ is much larger than $k_1 C_W$ and $(1 - \theta) \simeq 1$, the usual case in aquatic environments, the rate becomes first order with respect to C_W.

$$v = \frac{k_1}{k_{-1} + k_s} k_s R_T C_W \qquad (10)$$

Also, under these assumed steady-state conditions, C_W, and thus the rate, is proportional to C_T, the total reactant concentration.

Under the special condition that equilibrium sorption exists, i.e. k_{-1} is much greater than k_S, the first-order rate constant becomes equal to

$(K \cdot k_s \cdot R_T)$ where $K = k_1 / k_{-1}$. This K is sometimes referred to as the equilibrium constant of sorption, but it differs from the partition coefficients discussed in Section 2.1. It can be shown that, when reactant is very dilute, the fraction sorbed $\theta = K \cdot C_W$. Because $\theta \cdot R_T = C_R$, it follows that $K \cdot R_T = K_R$, the partition coefficient.

That the concentration dependence of a reaction rate in an aqueous particle suspension is described by a hyperbolic expression does not necessarily mean that the reaction occurs on a surface. Another kinetic model that does not involve a heterogeneous reaction can also be described by a hyperbolic rate expression that is equivalent to eq. 9. Consider a particle/water system in which some reactive species, X, undergoes reversible exchange between solution phase and the particle surface. This species reacts in solution phase with some reactant, M, that is added to the system.

$$S\text{--}X \underset{k_a}{\overset{k_d}{\rightleftharpoons}} X \qquad (11)$$

$$X + M \xrightarrow{k_X} \text{Products} \qquad (12)$$

If X is highly reactive, its concentration should reach a steady state shortly after reactant is added, a condition that is defined by:

$$C_X^{ss} = \frac{k_d \, C_{S\text{--}X}}{k_a + k_X \, C_M} \qquad (13)$$

where $C_{S\text{--}X}$ equals the concentration of sorbed reactant and C_M equals the concentration of M. For simplification we assume that $C_{S\text{--}X}$ is much larger than C_M and thus approximately constant throughout the reaction. The reaction rate is defined by:

$$v = k_X \, C_M \, C_X^{ss} \qquad (14)$$

where k_X is the bimolecular rate constant for the reaction. By substitution of eq. 13 into eq. 14, we obtain

$$v = \frac{k_d\, k_X\, C_{S--X}\, C_M}{k_a + k_X\, C_M} \qquad (15)$$

which is of the same general form as eq 9. A possible example of such a reaction is discussed in Section 3.2.

In the above considerations, the steady state approximation has been applied to define relationships that describe the reaction rate. This approximation is valid when concentrations of reaction intermediates, such as R in eq 5, remain approximately constant during reaction. In some systems, however, this may not be a valid assumption and non-steady-state kinetics apply. The exact solutions for a non-steady-state treatment of a variety of kinetic models have been derived (Moore and Pearson, 1981). These equations are cumbersome, however, and generally of little use. A more profitable approach involves the use of computer programs to analyze the kinetic data and calculate values for the rate constants that appear in the differential equations.

Based on this discussion, the saturation effect must always be assumed to occur in heterogeneous reactions, especially in those cases in which site-specific sorption is expected, e.g., partitioning that involves chemisorption or ion-exchange. The concentration of reactant required for saturation depends on properties of both the reactant and the particle and usually it is difficult to predict a priori.

The situation is complicated even further in systems involving reactions in natural sediment/water suspensions, because sediments are mixtures of competing sorbents. Saturation of reactive sites may occur at reactant concentrations that are much lower than those required to saturate sorption of the reactant on a sediment particle. Thus, an important first step of any study of chemical reactions in particle/water systems involves the determination of the dependence of the initial rate on reactant concentration.

2.3. Heterogeneous Reactions Involving Slow Interphase Transport

Two general diffusional processes are important in heterogeneous reactions. The first involves movement of the reactant molecules to and from the particle surface, and the second involves mass transport into and back out of particle interiors. If reaction is faster than these processes, then the equilibrium considerations discussed earlier, especially in Section 2.1, do not apply. In this section we mainly focus on kinetic models that have been used to analyze environmentally significant heterogeneous reactions in which intraparticle or interparticle transport is slow compared to reaction.

Diffusion to the particle surface becomes rate limiting when reaction on the particle is much more rapid than transport to and from the particle surface. This type of transport limitation has been considered in detail in various engineering publications (Satterfield and Sherwood, 1963). Pasciak and Gavis' (1975) treatment of transport limitation to nutrient uptake in lake microbiota provides other useful discussions and illustrations of this process.

The great industrial importance of heterogeneous catalysis has prompted numerous studies on the effects of pore diffusion and particle geometry on rates of catalytic reactions. The previously-mentioned text by Clark (1970) provides an introductory discussion and lead references to this research area.

Considerably less attention has been paid to diffusion effects on processes occurring on natural particles. In the remainder of this section we discuss the application of two models, the "two component" and the "dispersed kinetics" models, to the analysis of kinetics of processes in heterogeneous systems.

Studies by Karickhoff and co-workers (1980, 1984, 1985) of sorption processes involving sediments have provided much useful information concerning sorption kinetics. Using the gas purging of hydrophobic chemicals from sediment suspensions to examine desorption kinetics, Karickhoff and Morris (1985) found that

desorption can be factored into at least two components, a rapid release of "labile" sorbed chemical and a slower release of "nonlabile" sorbed chemical. The purged release of hexachlorobenzene (HCB) provides a good example (Figure 4). Karickhoff (1980) conceptualized the system using a model similar to eq. 1, assuming that loss of chemical was solely due to purging from the aqueous phase and that one of the particle phases, i.e. the "non-labile" phase, was accessed from water much more slowly than the other. He found that sorption to and desorption from the "nonlabile" phase of the particles could be described by a first order rate expression with rate constant, k_2. Based on detailed kinetic studies of four chemicals in equilibrated suspensions of several different sediments (Karickhoff and Morris, 1985), it was found that the following relation approximately described k_2 (Figure 5):

$$1/k_2 \text{ (hr)} = 0.03\ K_p \text{ (L/kg)} \qquad (16)$$

where K_p is the equilibrium partition coefficient corresponding to the ratio of concentrations of sorbed to dissolved chemical in the suspensions. The process quantified by k_2 involves sorption to or desorption from sediment components, probably particle interiors, that do not have direct access to water. Indeed, Wu and Gschwend (1985) have found that sorption kinetics involving natural sediments can be interpreted assuming diffusion of sorbate into pores of spherical particles.

Photolysis of the hydrophobic, aromatic hydrocarbon 1,1-bis(p-chlorophenyl)-2,2-dichloroethylene (DDE) in sediment suspensions (Zepp and Schlotzhauer, 1981) also involved diffusive rate limitations. Plots of log concentration versus time were linear for DDE photolysis in water, but in the sediment suspensions, the plots, like those for the purge of HCB (Figure 4), were nonlinear (Figure 6). The kinetic model shown in eq 1 was used to interpret the results, with W representing aqueous phase DDE, and R and U representing DDE sorbed in reactive

and unreactive phases, respectively. The results indicated that U was accessed much more slowly than R, thus accounting for the dependence of the photolysis kinetics on equilibration time prior to irradiation of the suspension. The aqueous and reactive phases were assumed to be in a rapid equilibrium that is described by the constant $F_R K_p$, where F_R is the fraction in phase R.

Comparisons of the kinetic analysis of the HCB purge and of the DDE photolysis strongly suggest that the "non-labile" and "unreactive" phases were approximately the same. Values of k_U evaluated from the DDE experiments (Table 1) (Zepp and Schlotzhauer, 1981) were the same as values of k_2 for HCB (Karickhoff and Morris, 1985) within a factor of 2, as was predicted by assuming that k_U can be computed using eq 16. The lack of photoreactivity for DDE sorbed in the unreactive phase could simply reflect a lack of light penetration into particle interiors or, alternatively highly efficient excited state quenching. That quenching could account for the results is supported by studies of DellaGuardia and Thomas (1983), who found that photoprocesses of a ruthenium complex were strongly quenched on various clay minerals. Kinetic analysis of the DDE data also indicated that the photolysis rate constant of DDE sorbed in phase R was 3 times greater than the rate constant in water (Table 1).

The nonlinear behavior exhibited in Figures 4 and 6 is by no means limited to processes involving natural sediments. Such behavior has been noted by De Mayo and co-workers (1985) in the case of pyrene fluorescence decay on silica gel surfaces, by Thomas and co-workers (1983, 1985) in the photoprocesses of tris(bipyridyl)ruthenium(II) cation sorbed on various clays, and by Brown and co-workers (1985) in the photoreduction of methylviologen cations sorbed on colloidal TiO_2. In all of the cases noted, the chemicals were tightly sorbed to the particle surface and interparticle or intraparticle transfer was much slower than the photoprocess. Typically, these kinetic data have been fit by a double exponential function.

Very recently, Albery and co-workers (1985) have developed another general kinetic model for the analysis of chemical reactions in heterogeneous systems. This "dispersed kinetics" model starts with two basic assumptions: (1) that heterogeneous reactions involve parallel reactions on multiple sites exhibiting different reactivities that can be described by a Gaussian distribution function and (2) that transport of reactant from one site to another is slow compared to reaction. When reaction is initiated, reactant molecules sorbed to the most reactive sites decay first, leaving an altered distribution of less reactive sorbed molecules. As a result, even though the reaction may be first-order with respect to reactant concentration for a given site, a log plot of total concentration versus time exhibits a decreasing slope with increasing conversion. To describe this system, Albery and coworkers (1985) assumed that the dispersion in rate constants could be described by a Gaussian distribution in ln (k) where k are the rate constants. The resulting integrated rate expression is:

$$\frac{C}{C_o} = \frac{1}{\pi^{1/2}} \int_{-\infty}^{+\infty} \exp(-x^2)\, \exp[-\tau \exp(\gamma x)]\, dx \qquad (17)$$

where C_o and C represent reactant concentration initially and at dimensionless time, $\tau (= \bar{k}\, t)$; $\exp(-x^2)$ is the normal distribution; and $\exp(\gamma x)$ expresses the dispersion ($\bar{k}$ is the mean rate constant and γ is a fitting parameter that describes the spread of the distribution.) If $\gamma = 0$ then there is no dispersion and eq 17 reduces to the simple first order rate expression:

$$C/C_o = \exp(-\tau) \qquad (18)$$

Examples of the use of this model are discussed by Albery and coworkers (1985) and by Brown and coworkers (1985) who analyzed kinetic data for photoinduced reductions on metal oxide surfaces.

2.4 Ecotoxicological Applications

The preceding sections have described models for reactions in heterogeneous

systems, ranging from the most generalizable models that deal with equilibrated systems to the most empirical systems in which reaction is much more rapid than interphase transport. Here we use the models to make general assessments of heterogeneous reactions of organic micropollutants on suspended particles and on particles in bottom sediments or soil/water mixtures.

Most organic micropollutants are nonionic, hydrophobic chemicals. As discussed by Karickhoff (1984) and Westall (1986), studies of equilibrium sorption of nonionic organic chemicals to sediments have shown that, at low concentrations of the chemical, the total sorbed concentration, C_S, is related to the aqueous phase concentration, C_W, by:

$$C_S = K_p C_W \qquad (19)$$

where K_p (expressed in this chapter in units of mL/g or L/kg) is the "sorption partition coefficient."

Sorption of nonionic organic chemicals to sediments mainly occurs on particles that are clay or silt sized. Moreover, sorption is strongly controlled by the organic carbon content of the sediment, although the organic component is typically only a minor fraction of the sediment mass. That is, for a given chemical on a series of sediments, K_{OC}, the ratio of K_p to the fractional organic carbon content of each sediment, f_{OC}, is approximately constant (Westall, 1986). The K_{OC} for a given organic chemical is approximately proportional to its octanol-water partition coefficient, K_{OW} (Karickhoff, 1984).

Veith (1985) has shown that the median value of K_{OW} for about 20,000 industrial chemicals regulated by the U.S Environmental Protection Agency is about 1000. This value corresponds to a K_{OC} of about 440 and to K_p values in the 5 to 50 range for sediments having f_{OC} in the range of 1% to 10%. Although nonionic organic micropollutants with K_p values in excess of 10,000 are not usual, such hydrophobic chemicals do enter the aquatic environment where, due

to their great tendency to bioconcentrate, they often cause serious problems. Examples include DDT, PCB's, dioxins and other notorious pollutants.

Assuming that sorption is governed by equilibrium relations, the relative effects of reactions on particles can be assessed using eq 20:

$$\frac{k_{obs}}{k_W} = \frac{F_W^e k_W + F_S^e k_S'}{k_W} \qquad (20)$$

where F_S^e is the total fraction sorbed, k_S' is the average rate constant in the sorbed state, k_{obs} is the rate constant for reaction in the particle suspension, and k_W is the rate constant in the absence of particles. The value of $\sum_i \rho_i K_i$, defined in terms of K_p values, is $(1 + \rho K_p)$, where ρ is the weight ratio of sediment to water. By combining eq 2 and eq 20:

$$\frac{k_{obs}}{k_W} = \frac{1}{1+\rho K_p}\left[1 + \rho K_p\left(\frac{k_S'}{k_W}\right)\right] \qquad (21)$$

Table 2 summarizes computed relationships (eq 21) between k_{obs}/k_W and k_S/k_W. Examination of this table leads to three main conclusions concerning environmental reactions of nonionic micropollutants on particle surfaces.

(1) For most nonionic micropollutants ($K_p \leq 50$), reaction on suspended particles is not likely to be significant. Suspended particle concentrations in lakes usually do not exceed 10 mg/L ($\rho = 10^{-5}$). Thus, the value of ρK_p for a typical nonionic organic chemical is expected to be no higher than about 0.001, i.e., only 0.1% is sorbed. For such a ρK_p, the rate constant in the sorbed state would have to be over three orders of magnitude larger than k_W in order for the overall reaction rate constants, k_{obs}, to be a factor of 2 greater than the rate constant for reaction in particle-free water (Table 2). In addition, chemical reaction also would have to be at least as rapid as other removal processes in order to be important. For example, the rate constant for epilimnetic water renewal in Lake Zurich is about 0.01 d^{-1} (Imboden and Schwarzenbach, 1985).

Thus, for a chemical with K_p = 50 L/kg, k_S for a photoreaction on the suspended particles in the epilimnion would have to be at least 10 d^{-1} to be significant. Such reactivity is not likely to be generally observed, although photoreactions of anilines on algal surfaces occur with rate constants in this range (Zepp and Schlotzhauer, 1983).

(2) For extremely hydrophobic chemicals with K_p values in excess of 10,000 L/kg (ρK_p in the range 0.1 to 1.0), the probability of reaction being significant on suspended particles is greatly enhanced. In addition, kinetic studies indicate that desorption lifetimes of such chemicals on sediments can be on the order of months (Figure 5), further enhancing the likelihood of reactions in the sorbed state.

(3) In bottom sediments and soils, the sorbent to water ratio ($\rho \geq 1$) is at least one million times greater than in the water column of a lake. Under these conditions most nonionic chemicals are predominantly sorbed and k_{obs}/k_W becomes approximately equal to k_S/k_W (Table 2). Reaction in the sorbed state has a much higher probability of being significant in such environments.

The above considerations apply to nonionic organic chemicals, but some important micropollutants are ionic. Organic cations, like metal ions, usually sorb very strongly to natural particles. For example, the dication, methylviologen, also known as paraquat, sorbs very tightly to clay sized particles; K_p typically exceeds 10^6 (Karickhoff and Brown, 1978). Methylviologen is known to be very susceptible to photoredox reactions on particles (Brown et al., 1985). Moreover, certain organic ligands, such as carboxylic acids, sorb strongly to metal oxides (Waite, 1985), thus enhancing the rate of metal dissolution (Stone and Morgan, 1986; Waite, 1985). Heterogeneous reactions of such ionizable organic chemicals are likely to be significant in water columns, as well as in bottom sediments or soils.

3. HETEROGENEOUS ORGANIC REACTIONS IN SEDIMENT SUSPENSIONS

This section emphasizes studies of hydrolysis and reduction, two major types of abiotic organic processes that are believed to be important in natural waters. The area of heterogeneous organic reactions involving metal oxides is discussed by Stone and Morgan (1986) elsewhere in this book. Useful discussions also are found among Theng's treatments of clay structure and interactions with organic polymers (Theng, 1979).

As used here, the term "abiotic" refers to processes that do not involve direct participation of metabolically active organisms. By this definition, abiotic processes include reactions involving chemicals of biological origin, such as extracellular enzymes or iron porphyrins. The results discussed here were obtained under conditions that isolated the abiotic from the biological processes. The isolation procedures used and their possible effects on sediment reactivity are discussed by Macalady et al. (1986).

3.1 Hydrolysis Reactions

The types of hydrolysis reactions of organic chemicals that have been studied include base-, neutral-, and acid-mediated reactions (Mabey and Mill, 1978; Wolfe, 1980; Perdue and Wolfe, 1983). The general rate expression for hydrolysis is:

$$v_{hy} = [\sum_i (k_{B,i}\, C_{B,i}) + k_N + \sum_i (k_{A,i}\, C_{A,i})]C \qquad (22)$$

where v_{hy} is the rate, $k_{B,i}$ and $C_{B,i}$ are rate constants and concentrations of bases, respectively, that mediate hydrolysis; k_N is the rate constant for neutral hydrolysis; and $k_{A,i}$ and $C_{A,i}$ are rate constants and concentrations, respectively, for acid hydrolysis. Perdue and Wolfe (1983) have shown that, for solution-phase abiotic hydrolysis reactions in aquatic environments, specific acid or base catalysis (by H+ and by OH-) is far more important than reactions mediated by other general acids and bases. Thus, the observed rate

constant, k_{hy} is expressed as:

$$k_{hy} = k_{ac}[H+] + k_N + k_b[OH-] \qquad (23)$$

At constant pH, the various terms, and the overall rate become pseudo-first-order with the contribution of a given hydrolysis process being dependent on the pH and the various rate constants. Changes in pH may result in changes in the observed hydrolysis rate constant that are reflected in a pH-rate profile. A variety of shapes describe pH-rate profiles for organic chemicals that enter aquatic environments. By judicious selection of pH and reactant, it is possible to conduct an experiment under conditions in which one of the three hydrolysis processes dominates. The remainder of this section provides examples of studies designed to determine the rates of these various types of hydrolysis processes for organic chemicals in sediment suspensions.

Neutral hydrolysis involves the pH-independent reaction of a chemical with water. Macalady and Wolfe (1984) have studied the neutral hydrolysis of six nonionic organic chemicals in suspensions of well-characterized sediments obtained from several U.S. water bodies. Under the short time domains used in the kinetic experiments, a simple one-site sorption model (eq. 1 in which U is ignored) could be used to analyze the kinetic results. Typical kinetic data for the neutral hydrolysis of the organophosphorothioate ester, chlorpyrifos, were discussed earlier (Figure 1). Computer analysis of these data indicated that k_S and k_W were very similar in magnitude. Similar results were obtained in suspensions of other sediments as well (Table 3). Studies such as these were also conducted for 5 other organic chemicals with the same general finding: neutral hydrolysis proceeded at about the same rate for nonionic organic chemicals dissolved in water or sorbed on sediments.

Studies also were conducted of the alkaline hydrolysis of chlorpyrifos at high pH values in sediment suspensions (Macalady and Wolfe, 1985). Changes

in the pH had no effect on the sorption partition coefficient of chlorpyrifos. In sharp contrast to the results for neutral hydrolysis, however, the sorbed chlorpyrifos reacted much slower than aqueous phase chlorpyrifos. The amount of retardation was close to that predicted using eq 4, assuming no reaction in the sorbed state.

Alkaline hydrolysis of hydrophobic esters also was strongly retarded when the esters were sorbed to sediments. This retarding effect is graphically illustrated in Figure 7, which compares the strongly sorbed octyl ester with the weakly sorbed methyl ester of 2,4-dichlorophenoxyacetic acid. The experiments were conducted by first equilibrating the sediment/water system for 3 days at pH 7 prior to jumping to pH 10. As discussed in Section 2.3, the curvature in the plot for the octyl ester also shows that the aqueous phase reaction occurred more rapidly than desorption. Note the similarities between Figures 4, 6, and 7.

In summary, the studies of hydrolysis on sediment surfaces have shown that sorption of nonionic organic chemicals to sediments has little effect on neutral hydrolysis which involves attack on reactant by water molecules. On the other hand, attack by hydroxide ions is strongly retarded. The retardation of alkaline hydrolysis was attributed to the destabilizing effect of the negative surface charge of sediments on the negatively charged transition state that mediates alkaline hydrolysis of esters. The hydrolysis results in sediments are strikingly similar to those reported for hydrolysis reactions of nonionic organic chemicals in other negatively charged particles designed to mimic biomembranes, e.g., micelles, vesicles (Fendler, 1975).

3.2 Organic Reductions in Anaerobic Sediment/Water Systems

Hydrophobic organic chemicals are often found in bottom sediments of lakes and in soils. In such environments, microbial activity sometimes greatly reduces

the concentration of dioxygen and the systems are said to be anaerobic. From past studies, it is known that several types of organic compounds are generally susceptible to reduction in anaerobic sediments: chlorinated hydrocarbons, nitroaromatic compounds, N- and O-alkylated organic compounds, azo compounds, and quinones, among others. A recent paper by Macalady and coworkers (1986) thoroughly discusses this work.

Few quantitative data are available on reductions of organic chemicals sorbed on sediments. A recent study by Sanders and Wolfe (1986), however, illustrates some of the models we discussed earlier. The reaction studied involved a 6-electron reduction of nitroaromatic compounds to the corresponding anilines in sterilized bottom sediments from local water bodies (Figure 8). Under the reaction conditions, the rate was first order with respect to nitroaromatic concentration and sediment concentration. For a series of alkyl-substituted nitrobenzenes, the rate constant decreased with increasing sorption K_p (Figure 9).

Sanders and Wolfe (1986) analyzed the kinetic results for the nitroaromatic reductions using a kinetic model similar to eq. 1 in which the reactant is partitioned between a reactive phase and an unreactive phase. The effect of partitioning into the unreactive phase was, as in the above-cited case of alkaline hydrolysis, to reduce the fraction of reactant in the reactive phase. Reaction was postulated to occur either at the particle/water interface or, alternatively, with a reductant released into the aqueous phase by the sediment. This latter mechanism was discussed in more detail in Section 2.2 (eq 11-12). The rate of reduction was reduced by 80 to 90% on heating, but it was unaffected by m-cresol, a reductive dehydrogenase enzyme blocking agent. These results indicate that catalysis by bioorganics or an extracellular enzyme(s) in the sediment may have been involved in the reduction. Similar effects have been

observed in kinetic studies of the reduction of methyl parathion, a nitroaromatic pesticide, in bottom sediments (Wolfe et al., 1985).

4. HETEROGENEOUS PHOTOREACTIONS

Particles in the upper layers of aquatic environments, on soil surfaces, and in water droplets in the atmosphere are exposed to sunlight. The particles in water bodies are among the most important sunlight absorbers and in many natural waters, the biota, detritus, and/or suspended sediments are almost completely responsible for light attenuation. No doubt a large portion of the solar radiation absorbed by these natural particles is converted into thermal energy, but a fraction of the absorbed radiation is diverted into photochemical reactions.

The widespread occurrence of photosynthetic organisms in aquatic environments is the most obvious evidence of the importance of heterogeneous photoreactions in water bodies. Recent research, however, has resulted in the discovery of other environmentally significant abiotic photoreactions involving particle surfaces. Also, heterogeneous photoreactions on metal oxide surfaces are increasingly being used as a method for wastewater and groundwater treatment.

The main goals of this section are two-fold. First, we supplement the general discussion of heterogeneous reactions presented above by a brief examination of some of the basic factors that govern heterogeneous photoreactivity. Secondly, we provide examples of various types of heterogeneous photoreactions that are believed to be of environmental significance.

4.1 Rate Equations and Types of Photoreactions

The rate of any type of photoreaction depends upon the rate of light absorption by the photoactive species, I_a, and the quantum efficiency of the reaction, ϕ. The rate of light absorption is affected, in turn, by the spectral overlap between the light source and the spectrum of the chemical that initiates the

photoreaction.

$$\text{Rate} = I_a \Phi \qquad (24)$$

The light absorption rate in a water body depends upon the solar spectral irradiance as it is transmitted down into the water and it also depends on the geometry of the light field. Particles in the photic zone influence the irradiance, and thus photolysis rates, through both light absorption and scattering (Miller and Zepp, 1979a; Smith et al., 1983). The concepts and terminology used in modeling the transmission of sunlight in natural waters are described in detail by Baker and Smith (1982), Morel and Smith (1982), and Jerlov (1976). The complex effects of light attenuation and scattering by sediments are illustrated by the interesting dependence of the direct photolysis rate of the ketone γ-methoxy-m-trifluoromethylbutyrophenone on the concentrations of various types of clays suspended in water (Figure 10). The photolysis of the ketone in these systems occurs completely in the aqueous phase. The enhancement in photolysis rate in some of the suspensions was attributed to increases in the mean light pathlength that were caused by scattering (Miller and Zepp, 1979a).

Photochemical processes at the particle/water interface can be subdivided into two main categories--direct and indirect. Direct photolysis processes involve the direct absorption of light by the sorbed substrate.

$$P + \text{light} \longrightarrow P^* \longrightarrow \text{Products} \qquad (25)$$

where P is some photoreactive substance on the particle surface and P* is the excited state that reacts to form products. On the other hand, heterogeneous photoreactions can also involve indirect photoprocesses, which are initiated through light absorption by photoreactive components of the particle, symbolized by sens because such substances are sometimes referred to as photosensitizers.

$$\text{sens} + \text{light} \longrightarrow \text{sens}^* \qquad (26)$$

$$\text{sens}^* + P \longrightarrow \text{Products} \qquad (27)$$

In some cases of indirect photolysis, no direct reaction occurs between the

excited surface component and the reactant, but rather the reaction involves short-lived intermediates derived from photolysis of the surface component. Indirect photoreactions involving the semiconductor mechanism are a special case that is discussed in more detail in Section 4.3.

4.2 Direct Heterogeneous Photoreactions

Considerable research has focused on heterogeneous photoreactions of iron oxides that apparently involve direct photolysis of inner sphere surface complexes of iron with various ligands (Faust and Hoffmann, 1985; Waite and Morel, 1984; Waite, 1985). Manganese oxides (Sunda et al., 1983) also undergo enhanced photoreductive dissolution in the presence of natural organic solutes. This research has been recently reviewed by Waite (1985). Waite and Morel (1984) have proposed a mechanism similar to eq 5 to account for the effects of various organic carboxylic acids on the photoreductive dissolution of the iron oxide, lepidocrocite (Figure 11). A similar model has been proposed by Faust and Hoffmann (1985) to describe the heterogeneous photooxidation of S(IV) species by the iron oxide, hematite.

Kinetic results obtained by Waite (1985), such as those in Figure 3, indicated that the rate of dissolution of lepidocrocite upon site saturation was about the same for four organic ligands, despite the fact that the solution-phase photolysis rates of iron (III) complexes of these ligands were quite different (Table 4). The extremely inefficient photoreduction of the iron oxide, goethite, in the presence of the weakly sorbed ethylene glycol, apparently involved an outer-sphere complex (Cunningham et al., 1985). Unlike carboxylic acids, ethylene glycol is incapable of forming inner sphere complexes with the iron oxide surface.

Several studies have appeared on the photolysis of organic chemicals sorbed on clay minerals or on natural sediments. These studies indicate that sorption of organic substrates on natural particles can result in significant

spectral shifts (DellaGuardia and Thomas, 1983; De Mayo et al., 1985; Gäb et al., 1977) along with changes in quantum efficiencies and photoproduct distributions (Nakamura and Thomas, 1985; Miller and Zepp, 1979b). Kinetic and product studies of photoreactions of extremely hydrophobic, sorbed nonionic organic chemicals indicated that the chemicals were in microenvironment that was less polar than water and that was a considerably better hydrogen donor (Miller and Zepp, 1979b). This result is consistent with sorption studies (Westall, 1986; Karickhoff, 1984) which indicate that such hydrophobic chemicals preferentially sorb in organic components of sediments.

4.3 Indirect Heterogeneous Photoreactions

Indirect photoreactions involving particles have also received considerable attention during the past few years. Most of this research can be subdivided into two broad areas: reactions involving reactive intermediates produced by surface photolysis, such as semiconductor-type mechanisms, and reactions involving electronically excited surface species.

Heterogeneous organic photocatalysis involving particles with semiconducting properties has received considerable attention recently. This research area has been reviewed by Fox (1983). Semiconductors such as titanium dioxide and zinc oxide have been shown to effectively catalyze both the reductions of halogenated chemicals and oxidation of various other pollutants (Carey and Oliver, 1980; Pruden and Ollis, 1983; Hidaka et al., 1985; Draper and Crosby, 1985).

All semiconductors have a characteristic optical band gap, which corresponds to the light energy required to promote an electron from the valence band to the conduction band. Several metal oxides that occur in the environment can be activated by absorption of ground level solar radiation (Table 5). When the electron is so promoted, it leaves behind a positively charged "hole" or vacancy in the conduction band. Oxidation of a reactant can occur through electron

transfer from reactant to hole on the surface. Likewise, reduction can occur on the surface through transfer of the promoted electron to reactant. Oxidation can also occur via reactions of the holes with water and the electrons with protons or oxygen to produce hydroperoxyl and hydroxyl radicals, which in turn can rapidly react with solution-phase reactant. The hydroperoxyl radicals also can react to form hydrogen peroxide. Studies of the photoproduction of H_2O_2 at zinc oxide surfaces date back to the early 1950's (Calvert et al., 1954).

Semiconductors are versatile reagents that show great promise for waste treatment. Their role in photochemistry in the aquatic environment appears to be very limited, however. For example, studies by Oliver and co-workers (1979) failed to find any photoproduction of hydroxyl radicals or chloroorganic photoreduction on various natural sediments and clay minerals. Leighton (1962) long ago reached much the same conclusion with regard to the role of semiconducting metal oxides in the formation of photochemical smog. Nonetheless, it appears possible that natural semiconducting particles may contribute to the photochemical generation of the oxidant, hydrogen peroxide, in the hydrosphere.

Surface photoreactions involving excited sensitizer molecules provide another indirect photolysis pathway. Humic substances, common constituents of natural particles, are known to photosensitize a variety of organic photoreactions (Zepp et al., 1985; Haag et al., 1984), including those mediated by singlet oxygen, an excited form of dioxygen. Recent studies by Gohre and Miller (1983, 1985) have confirmed that singlet oxygen photoproduction occurs on soil and other natural surfaces that are exposed to sunlight. Based on results of recent studies of sensitized reactions involving humic substances (Zepp et al., 1985), it is likely that future research will demonstrate that other types of surface photosensitized reactions involving excited triplet states occur as well.

The indirect photolysis of anilines and organophosphorothioates sorbed on algae provides another example that does not involve the intermediacy of singlet oxygen (Zepp and Schlotzhauer, 1983). The rate constants for these photoreactions were virtually unaffected by heat killing the cells and by addition of the metabolic inhibitor DCMU. The aniline reaction is described by the hyperbolic rate expression discussed in Section 2.2 (Figure 2). The reaction also exhibited a pronounced hydrophobic effect; rate constants for reaction of aniline, toluidine, and butylaniline were proportional to octanol/water partition coefficients for these compounds (Figure 12). This hydrophobic effect is exactly the opposite of that observed in the nitroaromatic reduction in anaerobic sediments (Figure 7), underscoring the interesting diversity of results obtained in kinetic studies of heterogeneous reactions.

5. CONCLUSIONS

The models and equations presented in this chapter provide a starting point for kinetic analysis of thermal and photochemical reactions in heterogeneous systems of environmental interest. Particularly under the short time domains used in laboratory studies, equilibrium concepts can sometimes be applied to describe the partitioning of the reactant between phases in sediment suspensions, e.g. in the case of the neutral hydrolysis of nonionic organic compounds.

Heterogeneous reactions, especially those of chemicals that sorb to particles by site-specific or chemisorption mechanisms, are often affected by site saturation. Under steady-state conditions such reactions are described by hyperbolic rate expressions; they can be first order or zero order with respect to reactant concentration (or some intermediate order) depending on reactant and particle concentration. Reductive photodissolutions of metal oxides and indirect photoreactions on algae surfaces are two types of reactions that involve site saturation.

Reactions in heterogeneous systems also can be affected by intraparticle or interparticle transport. Such transport effects are particularly likely to occur in the case of tightly sorbed organic cations such as methyl viologen, also known as paraquat, or in the case of extremely hydrophobic nonionic organic reactants that have been equilibrated for long time periods prior to initiation of reactions such as photolysis or alkaline hydrolysis. Semilog plots of concentration versus time for such reactions are usually characterized by a decrease in slope with increasing conversion. Two-component or dispersed kinetics models are used to treat the kinetic results in these systems.

Through application of these concepts, it was shown that the neutral hydrolysis rates of various organic chemicals are approximately unaffected by sorption on certain sediments, but that the alkaline hydrolysis rates of esters are strongly retarded by sediment sorption. In anaerobic sediment/water systems, the reduction rates of nitroaromatic compounds exhibit sorptive retardation, an effect that is possibly attributable to competition between sorption to unreactive sediment components and reaction with some reductant in the aqueous phase.

Photoreaction rates in particle/water systems are influenced by effects of the particles on the irradiance, by the fraction of the reactant that is sorbed on photoreactive sites, and by the quantum efficiency of the photoreaction on the particle surface. Two types of surface photoreactions occur, those involving direct light absorption by the sorbed reactant and those involving initiation of photolysis through light absorption by photoreactive components of the particle. Photoreactions of surface inner sphere complexes between metal oxides and organic ligands provide examples of important direct reactions. Reactions involving semiconductor mechanisms, e.g. TiO_2 mediated oxidations, and photosensitized reactions on surfaces, e.g. surface photooxidations

involving singlet oxygen, are two types of indirect photoprocesses that are relevant to wastewater treatment or enviromental organic oxidations.

ACKNOWLEDGEMENTS

We appreciate the many helpful discussions with S.W. Karickhoff concerning sorption kinetics and kinetics in heterogeneous systems. We also thank A.T. Stone, T.D. Waite and P. Gschwend for prepublication copies of manuscripts that were discussed here, and B.C. Faust for a copy of his dissertation and other reference sources.

LITERATURE CITED

W.J. Albery, P.N. Bartlett, C.P. Wilde, and J.R. Darwent, A general model for dispersed kinetics in heterogeneous systems, J. Am. Chem. Soc., 107, 1854-1858 (1985).

K.S. Baker and R.C. Smith, Bio-optical classification and model of natural waters 2, Limnol. Oceanog., 27, 500-509 (1982).

G.T. Brown, J.R. Darwent, and P.D.I. Fletcher, Interfacial electron transfer in TiO_2 colloids, J. Am. Chem. Soc., 107, 6446-6451 (1985).

J.G. Calvert, K. Theurer, G.T. Rankin, W.M. MacNevin, A study of the mechanism of the photochemical synthesis of hydrogen peroxide at zinc oxide surfaces, J. Am. Chem. Soc., 76, 2575-2578 (1954).

J.H. Carey and B.G. Oliver, The photochemical treatment of wastewater by ultraviolet irradiation of semiconductors, Water Poll. Res. J. of Canada, 15, 157-185(1980).

A. Clark, The Theory of Adsorption and Catalysis, Academic Press, New York (1970), pp. 233-401.

K.M. Cunningham. M.C. Goldberg, and E.R. Weiner, The aqueous photolysis of ethylene glycol adsorbed on goethite, Photochem. Photobiol., 41, 409-416 (1985).

R.A. DellaGuardia and J.K. Thomas, Photoprocesses on colloidal clay systems. Tris(2,2'-bipyridine)ruthenium(II) bound to colloidal kaolin and montmorillonite, J. Phys. Chem., 87, 990-998(1983).

P. De Mayo, L.V. Natarajau, and W.R. Ware, Surface photochemistry: temperature effects on the emission of aromatic hydrocarbons adsorbed on silica gel, in M.A. Fox, Ed., Organic Phototransformations in Nonhomogeneous Media, ACS Symposium Series, Washington, D.C., 1985, pp. 1-19.

R.B. Draper, Jr. and D.G. Crosby, Enhanced photodegradation of thiocarbamate herbicides, presented in part at the 189th National Meeting of the American Chemical Society, Miami, FL, April 1985.

B.C. Faust and M.R. Hoffmann, Photo-induced dissolution of hematite by S(IV) oxyanions, Environ. Sci. Technol., in press.

J.H. Fendler and E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975.

M.A. Fox, Organic heterogeneous photocatalysis: Chemical conversions sensitized by irradiated semiconductors, Acc. Chem. Res., 16, 314-321(1983).

S. Gäb, J. Schmitzer, H.W. Thamm, H. Parlar, and F. Korte, Photomineralisation rate of organic compounds adsorbed on particulate matter, Nature, 270, 331-333 (1977).

G.L. Gaines, Jr. and G. Wise, Insiders, outsiders, and surfaces: Irving Langmuir's contribution to catalysis, in B.M. Davis and W.P. Hettinger, Jr., Ed., Heterogeneous Catalysis: Selected American Histories, ACS Symposium Series 222, Washington, D.C., 1983, pp. 13-22.

K. Gohre and G.C. Miller, Singlet oxygen generation on soil surfaces, J. Ag. Food Chem., 31, 1104-1108(1983).

K. Gohre and G.C. Miller, Photochemical generation of singlet oxygen on non-transition-metal oxide surfaces, J. Chem. Soc., Faraday Trans. 1, 81, 793-800 (1985).

W.R. Haag, J. Hoigné, E. Gassman, and A.M. Braun, Singlet oxygen in surface waters - Part II: Quantum yields of its production by some natural humic materials as a function of wavelength, Chemosphere, 13, 641-650(1984).

H. Hidaka, H. Kubota, M. Graetzel, N. Serpone, and E. Pelizetti, Photodegradation of the sodium dodecylbenzene-sulfonate surfactant in aqueous semiconductor dispersions, Nouv. J. Chim., 9, 67-69(1985).

D.M. Imboden and R.P. Schwarzenbach, Spatial and temporal distribution of chemical substances in lakes: modeling concepts, in W. Stumm, Ed., Chemical Processes in Lakes, Wiley, New York, 1985, pp. 1-30.

N. Jerlov, Marine Optics, Elsevier, Amsterdam (1976).

S.W. Karickhoff, Sorption kinetics of hydrophobic pollutants in natural sediments, in R.A. Baker, Ed., Contaminants and Sediments, Vol. II, Ann Arbor Science, Ann Arbor, Mich. (1980), pp. 193-205.

S.W. Karickhoff, Organic pollutant sorption in aquatic systems, J. Hydraul. Eng., 110, 707-735(1984).

S.W. Karickhoff and D.S. Brown, Paraquat sorption as a function of particle size in natural sediments, J. Environ. Qual., 7, 246-252 (1978).

S.W. Karickhoff and K.R. Morris, Sorption dynamics of hydrophobic pollutants in sediment suspensions, Environ. Toxicol. Chem., 4, 469-479 (1985).

K.J. Laidler and P.S. Bunting, The Chemical Kinetics of Enzyme Action, Clarendon Press, London(1973), pp.382-412.

P. Leighton, Photochemistry of Air Pollution, Academic Press, New York (1961), pp. 96-98.

W. Mabey and T. Mill, Critical review of hydrolysis of organic compounds in water under environmental conditions, J. Phys. Chem. Ref. Data, 7, 383 (1978).

D.L. Macalady, P.G. Tratynek, and T.J. Grundl, Abiotic reduction reactions of anthropogenic organic chemicals in anaerobic systems: A critical review, J. Hydrol. Contam., in press.

D.L. Macalady and N.L. Wolfe, Abiotic hydrolysis of sorbed pesticides, in R.F. Krueger and J.N. Seiber, Ed., Treatment and Disposal of Pesticide Wastes, ACS Symposium Series 259, Washington D.C, 1984, pp. 221-244.

D.L. Macalady and N.L. Wolfe, Effects of sediment sorption on abiotic hydrolyses. I. Organophosphorothioate esters, J. Agr. Food Chem., 33, 167-173 (1985).

G.C. Miller and R.G. Zepp, Effects of suspended sediments on photolysis rates of dissolved pollutants, Water Res., 13, 453-459 (1979a).

G.C. Miller and R.G. Zepp, Photoreactivity of aquatic pollutants sorbed on suspended sediments, Environ. Sci. Technol., 13, 860-863 (1979b).

J.W. Moore and R.G. Pearson, Kinetics and Mechanism, John Wiley and Sons, New York (1981), pp.284-333.

A. Morel and R.C. Smith, Terminology and units in optical oceanography, Mar. Geodesy, 5, 335-349 (1982).

T. Nakamura and J.K. Thomas, Photochemistry of materials adsorbed on clay systems. Effect of the nature of the adsorption on the kinetic description of the reactions, Langmuir, 1, 568-573 (1985).

B.G. Oliver, E.G. Cosgrove, and J.H. Carey, Effect of suspended sediments on the photolysis of organics in water, Environ. Sci. Technol., 13, 1075-1077 (1979).

W.J. Pasciak and J. Gavis, Transport limited nutrient uptake rates in Ditylum brightwellii, Limnol. Oceanog., 20, 604-617 (1975).

E.M. Perdue and N.L. Wolfe, Prediction of buffer catalysis in field and laboratory studies of pollutant hydrolysis reactions, Environ. Sci. Technol., 17, 635-642 (1983).

A.L. Pruden and D.F. Ollis, Degradation of chloroform by photoassisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide, Environ. Sci. Technol., 17, 628-631 (1983).

P. Sanders and N.L. Wolfe, Reduction of nitroaromatic compounds in anaerobic, sterile sediments, presented in part at the 190th National Meeting of the American Chemical Society, Chicago ILL, Sept. 1985.

C.N. Satterfield and T.K. Sherwood, The Role of Diffusion in Catalysis, Addison--Wesley, Reading, Mass. (1963).

R.C. Smith, K.S. Baker, and J.B. Fahy, Effects of suspended sediments on penetration of solar radiation into natural waters, U.S. Environmental Protection Agency Report EPA-600/S3-83-060, Sept. 1983, NTIS Order No. PB 83-238 188.

A.T. Stone, Adsorption of organic reductants and subsequent electron transfer on metal oxide surfaces, in J. A. Davis, Ed., Surface Processes in Aqueous Geochemistry, ACS Symposium Series, Washington, D.C., 1985, submitted for publication.

A.T. Stone and J.J. Morgan, Reductive dissolution of metal oxides, Chapter _____ in this book.

W.H. Strehlow, and E.L. Cook, Compilation of energy band gaps in elemental and binary compound semiconductors and insulators, J. Phys. Chem. Ref. Data, 2, 163-199 (1973).

W.G. Sunda, S.A. Huntsman, and G.R. Harvey, Photoreduction of manganese oxides in seawater and its geochemical and biological implications, Nature, 301, 234-236 (1983).

B.K.G. Theng, Formation and Properties of Clay-polymer Complexes, Elsevier, New York (1979).

G. Veith, U.S. Environmental Protection Agency, Duluth, MN, personal communication, 1985.

T.D. Waite, Photoredox chemistry of colloidal metal oxides, in J.A. Davis, Ed., Surface Processes in Aqueous Geochemistry, ACS Symposium Series, Washington D.C., 1985, submitted for publication.

T.D. Waite and F.M.M. Morel, Photoreductive dissolution of colloidal iron oxide: effect of citrate, J. Colloid Interface Sci., 102, 121(1984).

J.C. Westall, Adsorption mechanisms in aquatic chemistry, Chapter ___ in this book.

N.L. Wolfe, Determining the role of hydrolysis in the fate of organics in natural waters, in R. Haque, Ed., Dynamics, Exposure, and Hazard Assessment of Toxic Chemicals, Ann Arbor Science, Ann Arbor, Mich. (1980), pp. 163-177.

N.L. Wolfe, B.E. Kitchens, D.L. Macalady, and T.J. Grundl, Physical and chemical factors that influence the anaerobic degradation of methyl parathion in sediment systems, submitted to Environ. Toxicol. Chem., 1985.

S. Wu and P.M. Gschwend, Sorption kinetics of hydrophobic organic compounds to natural sediments and soils, submitted to Environ. Sci. Technol.

R.G. Zepp, Photobiological transformations of xenobiotics in natural waters: role of microalgae, presented in part at the 189th National Meeting of the American Chemical Society, Miami, Fla. (1985).

R.G. Zepp and D.M. Cline, Rates of direct photolysis in aquatic environments, Environ. Sci. Technol., 11, 359-366 (1977).

R.G. Zepp and P.F. Schlotzhauer, Effects of equilibration time on photoreactivity of the pollutant DDE sorbed on natural sediments, Chemosphere, 10, 453-460 (1981).

R.G. Zepp and P.F. Schlotzhauer, Influence of algae on photolysis rates of chemicals in water, Environ. Sci. Technol., 17, 462-468 (1983).

R.G. Zepp, P.F. Schlotzhauer, and R. Merritt Sink, Photosensitized transformations involving electronic energy transfer in natural waters: role of humic substances, Environ. Sci. Technol., 19, 74-81 (1985).

Table 1. Kinetic parameters for the photolysis (313 nm) of DDE sorbed on clay-sized particles of soil and sediment (Zepp and Schlotzhauer, 1981)

parameter[a]	Ohio soil	Ohio River sediment	Mississippi River sediment
F_R^e	0.56	0.62	0.43
k_u, h^{-1}	5.8×10^{-3}	4.7×10^{-3}	3.7×10^{-3}
k_S/k_W	3.2	not determined	3.1

[a]See eq 1-4 for definition.

Table 2. Estimated reaction rates in equilibrated particle/water systems (eq 21)

		$\frac{k_{obs}}{k_W}$ [a]		
k_S'/k_W	ρK_p =	10^{-5}	10^{-3}	1
0.1		1.00	1.00	0.60
1		1.00	1.00	1.50
10		1.00	1.0	10.5
100		1.00	1.10	100
1000		1.01	2.00	1000

[a]Estimated ratio of rate constant in particle suspension to rate constant in particle-free water.

Table 3. Kinetic data for neutral hydrolysis of selected nonionic organic chemicals in sediment suspensions (Macalady and Wolfe, 1984) (at 35°C unless indicated otherwise)

chemical	sediment	ρ	fraction sorbed	k_{hy}, min^{-1}	k_W, min^{-1}	k_S, min^{-1}
chlorpyrifos	EPA-14	0.20	0.94	1.0×10^{-5}	1.0×10^{-5}	6.9×10^{-6}
	EPA-23	0.016	0.87	1.6×10^{-5}	1.0×10^{-5}	1.2×10^{-5}
diazinon	EPA-26	0.040	0.64	3×10^{-5}	3.8×10^{-5}	2.9×10^{-5}
Ronnel	EPA-26	0.040	0.96	2.7×10^{-5}	3.8×10^{-5}	2.6×10^{-5}
benzyl chloride[a]	EPA-13	0.025	0.05	1.4×10^{-3}	1.25×10^{-3}	--
	EPA-2	1.0	0.87	1.15×10^{-3}	1.21×10^{-3}	--
4-(p-chlorophenoxy)-butyl bromide	EPA-12	0.050	0.80	--	7.9×10^{-5}	5.1×10^{-5}
hexachloro-cyclopentadiene[b]	EPA-13	0.20	--	2.2×10^{-4}	--	--
		1.0	--	2.0×10^{-4}	--	--
		2.0	--	1.3×10^{-4}	--	--

[a]at 25°C; [b]at 30°C.

Table 4. Kinetic parameters that describe photodissolution (365 nm) of γ-FeOOH in aqueous solutions (pH 4, 0.01 M NaCl) of selected organic carboxylic acids (Waite, 1985) (see eq 5-9)

organic acid	k_{soln}, min^{-1} [a]	k_S, min^{-1} [b]	$\frac{k_1}{k_{-1} + k_S}$, M^{-1}
Tartaric	0.49	0.032	$10^{6.6}$
Citric	0.27	0.028	$10^{5.7}$
Oxalic	0.63	0.034	$10^{5.3}$
Salicylic	0.67	0.030	$10^{4.1}$
Phthalic	0.14	---	---

[a]Photolysis rate constant for Fe(III) complex in solution; [b]rate constant for photoreduction step in dissolution of γ-FEOOH.

Table 5. Band gap energies for selected semiconducting oxides that absorb sunlight (Strehlow and Cook, 1973)

Oxide	Band gap, eV	Wavelength of light equivalent to band gap, nm
ZnO	3.35	370
PbO	2.76	499
TiO_2 (rutile)	3.0 - 3.3	376 - 413
β-MnO_2	0.26	4770
β-PbO_2	1.7	729
α-Fe_2O_3 (hematite)	2.34	530
CdS	2.4	517
β-HgS	0.54	2300

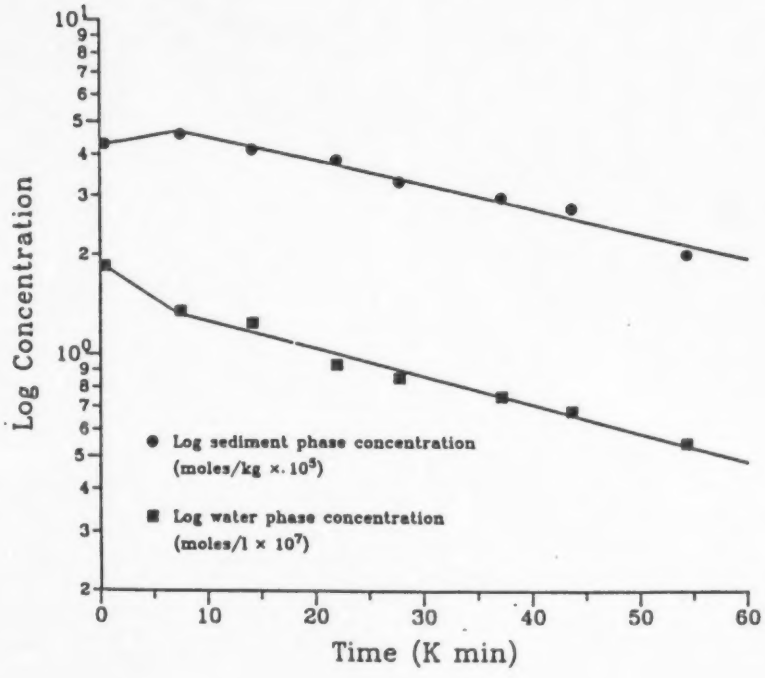


Figure 1. Chlorpyrifos hydrolysis in aqueous suspension of sediments (Macalady and Wolfe, 1985).

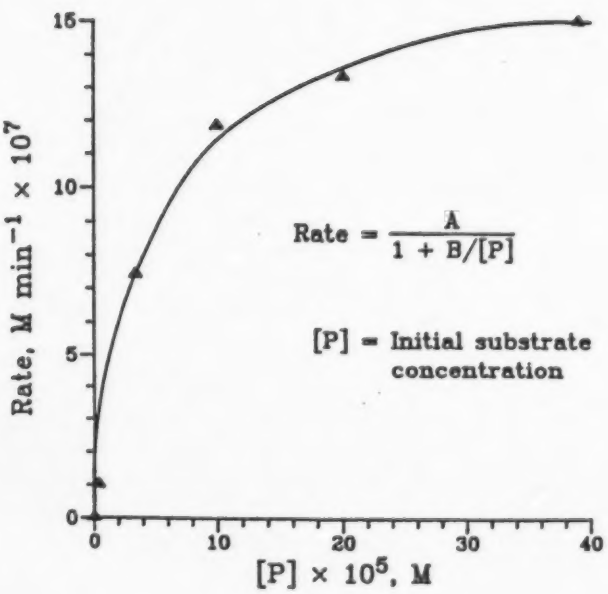


Figure 2. Rate versus substrate concentration in the sunlight-induced oxidation of aniline in suspension of Chlamydomonas sp. (Zepp and Schlotzhauer, 1983).

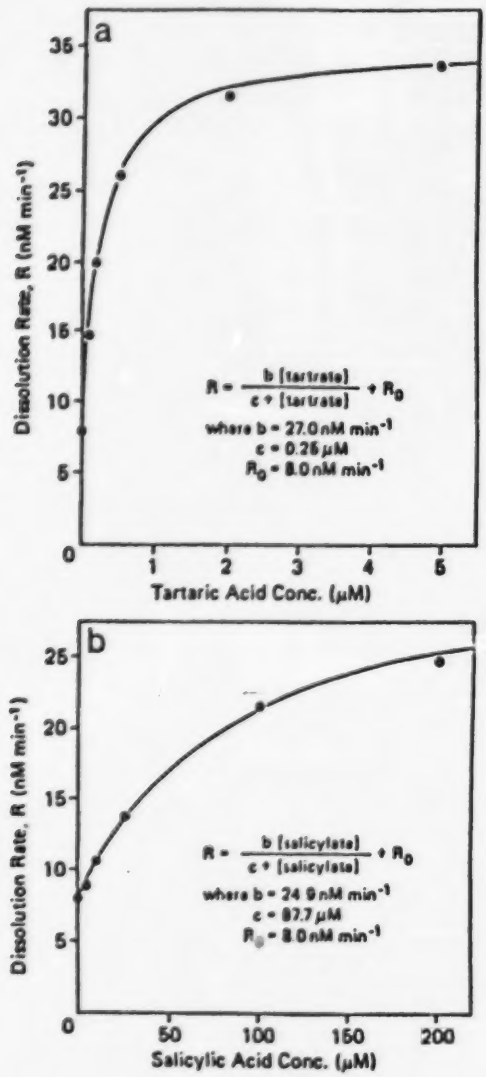

a
Dissolution Rate, R (nM min⁻¹)
Tartaric Acid Conc. (μM)
R = b [tartrate] / c + [tartrate] + R0
where b = 27.0 nM min⁻¹
c = 0.26 μM
R0 = 8.0 nM min⁻¹
b
Dissolution Rate, R (nM min⁻¹)
Salicylic Acid Conc. (μM)
R = b [salicylate] / c + [salicylate] + R0
where b = 24.9 nM min⁻¹
c = 87.7 μM
R0 = 8.0 nM min⁻¹

Figure 3. Dependence of the dissolution rate of 5 μM γ-FeOOH (pH 4.0, 0.01 M NaCl) on concentration of tartaric and salicylic acid (used with permission of Waite, 1985).

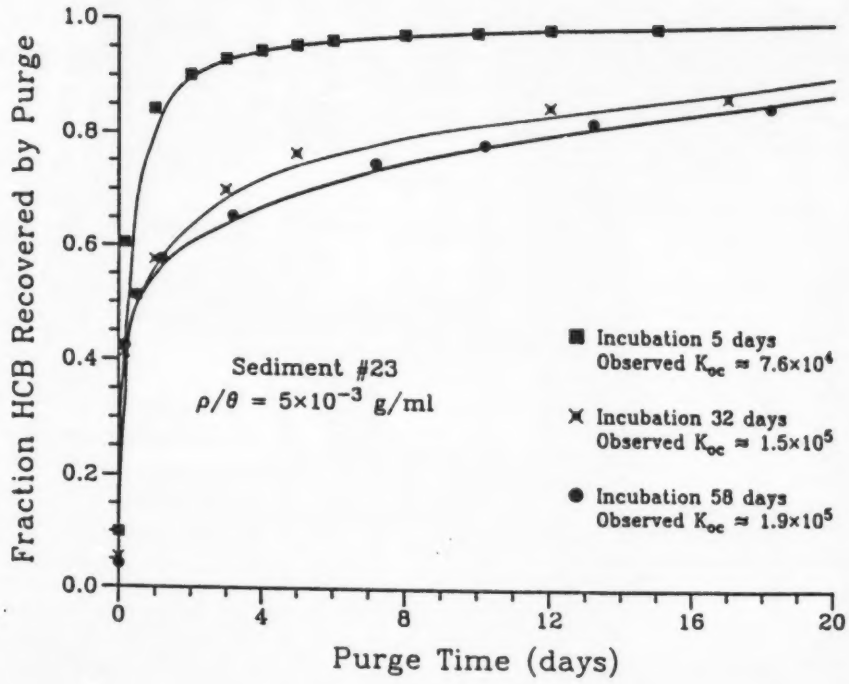


Figure 4. Purged volatilization of hexachlorobenzene from sediment suspension in water (Karichoff, 1984).

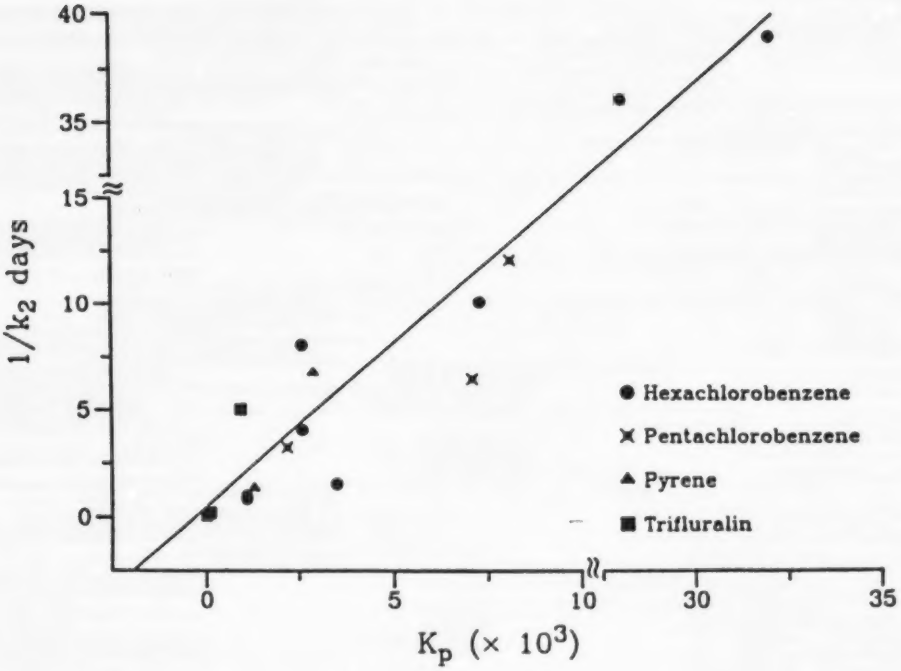


Figure 5. Dependence of nonlabile release constant (k_2) on sorption equilibrium constant (K_p) (Karickhoff and Morris, 1985).

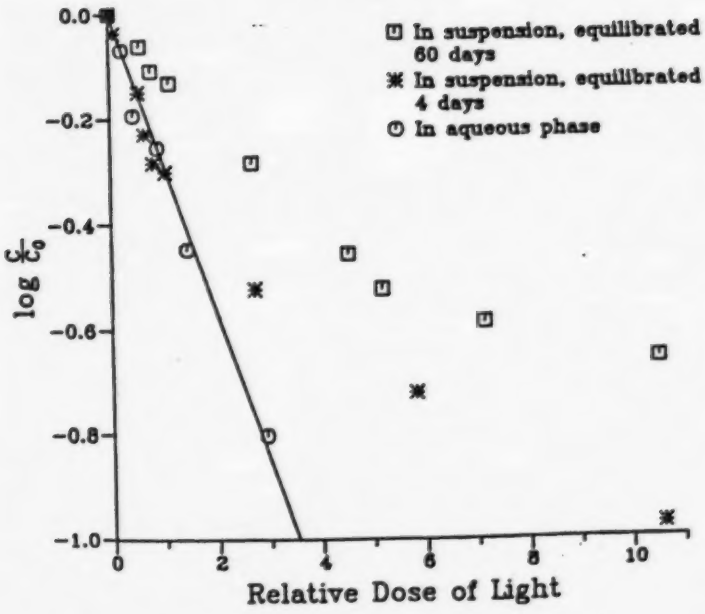


Figure 6. Photoreaction of 2,2-dichloro-1,1-bis(p-chlorophenyl)ethylene(DDE) in aqueous suspension of Ohio River sediments and in supernatant of centrifuged sediment suspension (Zepp and Schlotzhauer, 1981).

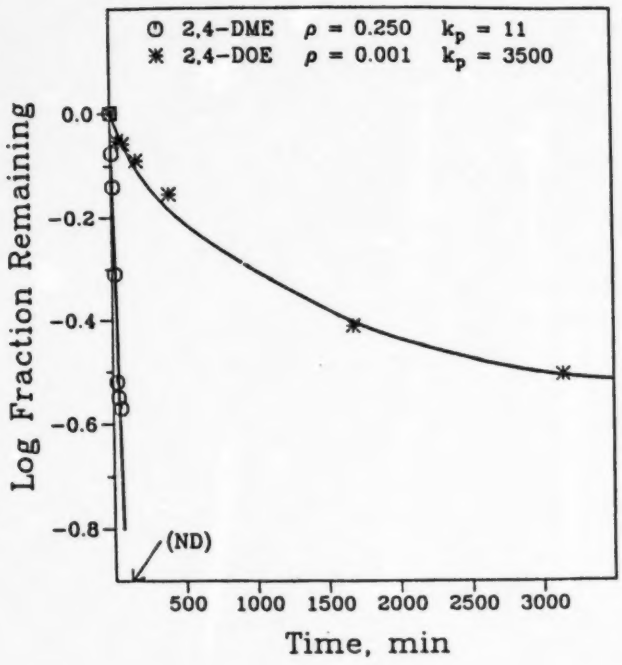
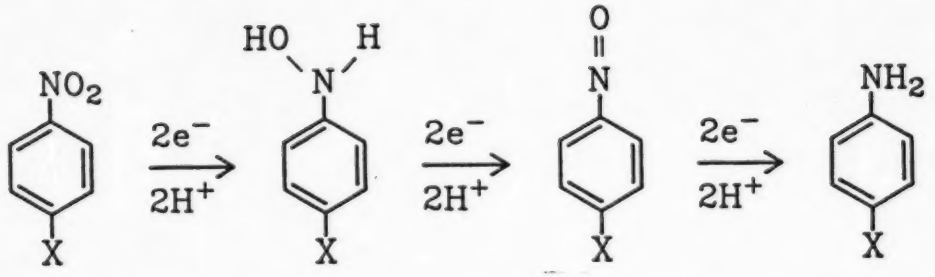


Figure 7. Comparison of alkaline hydrolysis (pH 10) of the methyl ester of 2,4-dichlorophenoxyacetic acid (2,4-DME) with its octyl ester (2,4-DOE) in sediment suspension (Macalady and Wolfe, 1984).



X = H−, Et−, *n*−Butyl−, or *n*−Octyl−

Figure 8. Reduction of nitroaromatic compounds in anaerobic sediments (Sanders and Wolfe, 1985).

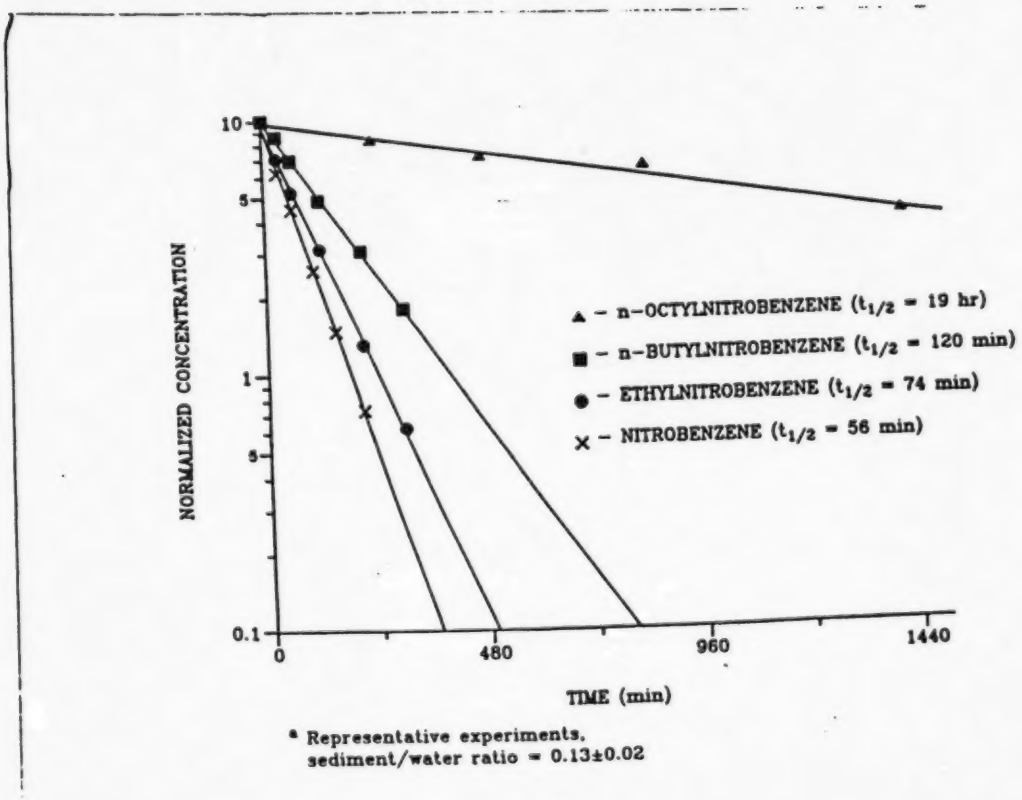


Figure 9. Kinetic data for reaction of nitroaromatic compounds in anaerobic sediments (Sanders and Wolfe, 1985).

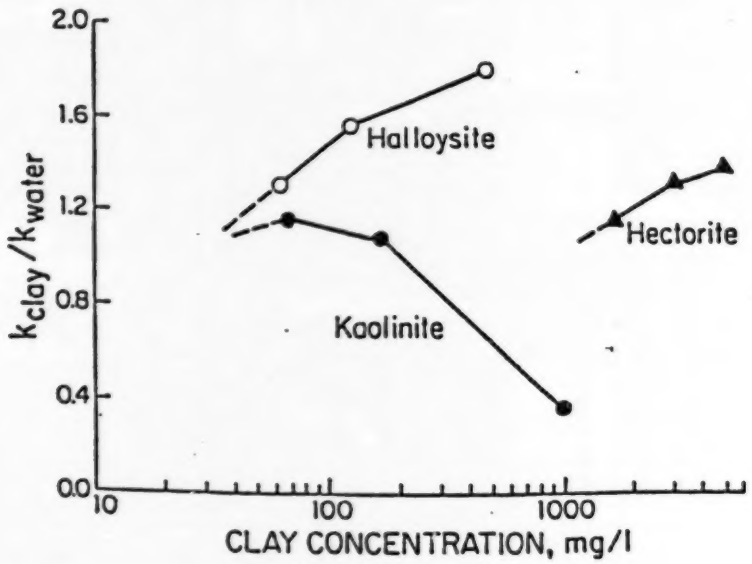


Figure 10. Direct photolysis of γ-methoxy-m-trifluoromethylbutyrophenone in aqueous suspensions of clay minerals. k_{clay} and k_{water} are first-order rate constants in clay suspension and in distilled water, respectively. Substrate is over 95% dissolved in solution phase in all cases (Miller and Zepp, 1979a).

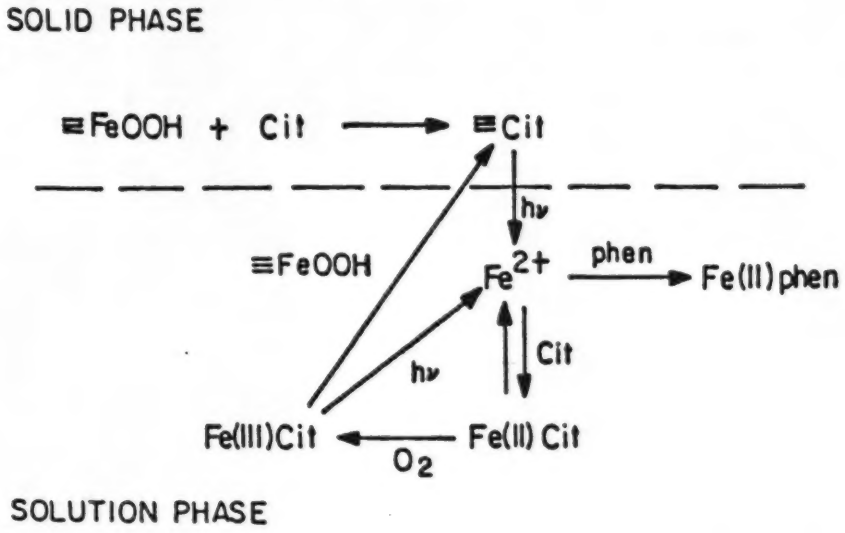


Figure 11. Model for major processes occurring in irradiated suspensions of iron oxides in aqueous citrate solutions (used with permission of Waite and Morel, 1984).

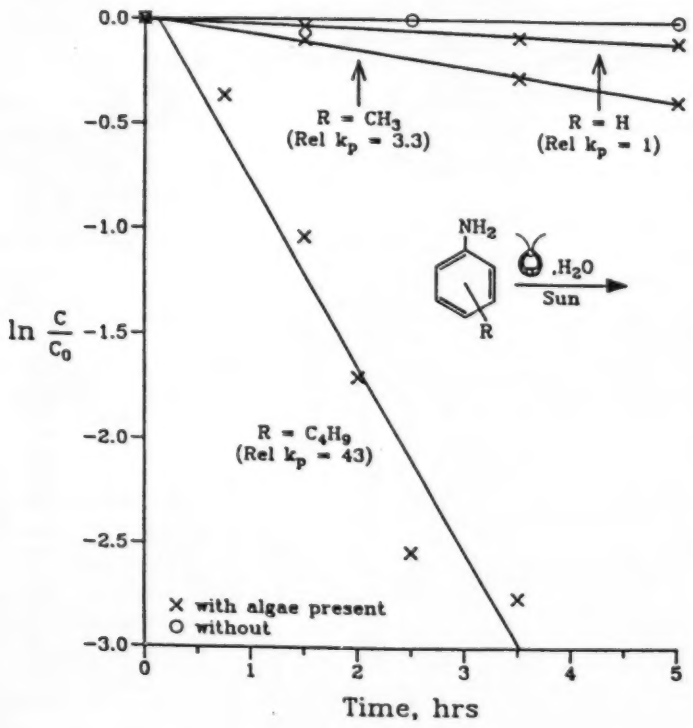


Figure 12. Kinetic plots for heterogeneous oxidation of aniline and alkyl-substituted anilines in suspensions of Chlamydomonas sp. (Zepp, 1985).